

**THE INHIBITION OF VAPOR-PHASE
CORROSION: A REVIEW**

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By

G.E. Fodor

**Belvoir Fuels and Lubricants Research Facility (SwRI)
Southwest Research Institute
San Antonio, Texas**

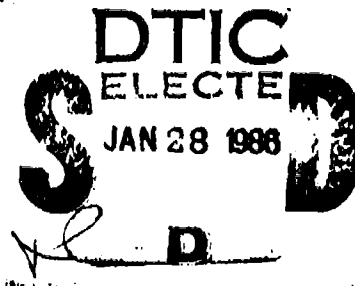
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FOREWORD

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I. INTRODUCTION

The direct cost of atmospheric corrosion of metals and alloys in the United States alone has been estimated^{1,2} to be between \$5 billion to over \$20 billion annually. This atmospheric corrosion, known by some researchers^{**} as vapor phase corrosion (VPC), is due to the individual and combined action of oxygen, moisture, and atmospheric pollutants.^{*} Additional contributors to VPC are rain, snow, dust, soot, ash, wind, and radiation (light, heat, etc.). The rate of VPC may be accelerated by both acids and bases, depending upon the metal.

Rosenfeld³ showed that the mechanism of this attack is electrochemical, in which the electrolyte is composed of a thin film of humidity on the surface of the metal. It has been shown for iron that when relative humidity is below 60 percent, no corrosion is expected, while above 75 to 80 percent, the degree of corrosion will be high.

Detrimental effects caused by photochemical reactions of sulfur dioxide and nitrogen oxides have been demonstrated by Stern.⁶

Classical methods of protecting equipment from atmospheric attack include (a) using coating materials or paints and (b) alloying the metal to increase its resistance to corrosion. An effective and relatively inexpensive method of controlling VPC in closed environments is through the use of vapor phase corrosion inhibitors (VCI). These materials, while having an appropriate vapor pressure, possess "high passivating properties, strong tendencies toward surface adsorption, and the ability to form a comparatively strong and stable bond with the metal surface."³

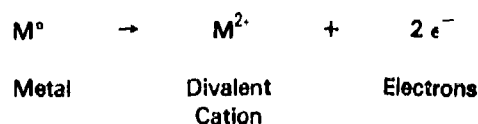
* Superscript numbers refer to the references at the end of this report.

** Some researchers limit "vapor phase corrosion" to mean an attack in a closed space while "atmospheric corrosion" refers to corrosion in the open air.

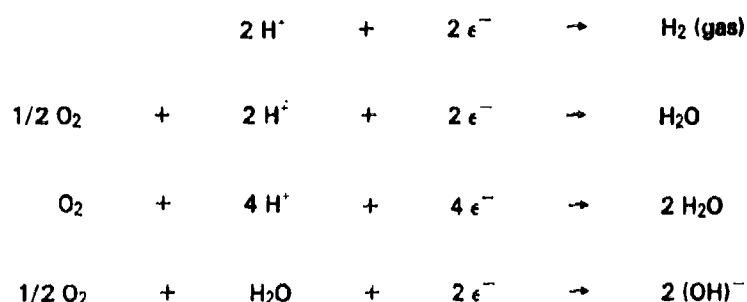
II. DEFINITION AND CLASSIFICATION OF INHIBITORS

General electrochemical reactions may be written to describe corrosion that may take place at the anode and at the cathode. For a divalent metal, the following equations may be written:

Anodic Oxidation:



Cathodic Reduction:



All corrosion takes place at the anode, where the metal, M^0 , loses electron(s) and becomes a positive ion. This oxidation will proceed only if the produced electrons and ions are removed at the cathode. These reactions occur as anode-cathode reaction pairs, and each is called a "half-cell reaction."

Each half-cell reaction has a half-cell potential associated with it. These electrode potentials vary with concentration of the reacting species of the electrolyte and the temperature.

For the reaction



where l is the number of moles of substance L , m is the number of moles of substance M , etc. The electrode potential, E , of the reaction is given by the Nernst equation:

$$E = E_0 + 2.3 \frac{RT}{nF} \log \frac{(a_O)^o (a_P)^p}{(a_L)^l (a_M)^m}$$

where E_0 is the electrode potential when all reactants are in their standard states (i.e., at unit activity), R is the gas constant, T is the absolute temperature, n is the number of electrons transferred in the reaction, F is the Faraday constant, a_O is the activity of substance O , a_P is the activity of substance P , etc. For example, in the case of iron corroding to form ferrous ion according to



the electrode potential is given by

$$E = -0.440 + 2.3 \frac{RT}{2F} \log \frac{(Fe^{++})}{(Fe)}$$

Since solid iron is at unit activity, the electrode potential of this reaction increases (becomes more positive) as the activity (or concentration) of ferrous ion in solution increases.

The electrode potential is measured as a difference between that of the half-cell reaction in question and the standardized hydrogen electrode ($H_2 \rightarrow 2H^+ + 2e^-$). More positive E values mean more anodic character; and, therefore, easier oxidizability or higher tendency toward corrosion. Since anode and cathode reactions must be in equilibrium, limiting either of these processes will retard the overall reaction. Accordingly, corrosion inhibitors may retard either the anode or cathode reactions, or both.

Fischer⁷ defines "inhibition as a diminution of the mean rate of chemical reactions and/or of physical processes by material influence. Preferentially, the concept of inhibition is used in phase-boundary reactions (or processes). Inhibition then is caused by one or more substances assembling in or near the phase boundary of a two-phase (or rarely a three-phase) system." According to this definition, oxide layers or varnish films may not be considered inhibitors.

Fischer also offered a classification of inhibitors.⁸ According to this classification, the categories of corrosion inhibitors are:

- a. interface inhibitors that influence chemical processes immediately at the metal/electrolyte interface, and
- b. membrane-inhibitors, in which the effect is caused by "a porous but coherent polymolecular or polymeric layer covering the interface of the electrode." This is a special case of interface inhibition, but with thicker layers.
- c. electrolyte-layer inhibitors, that alter the processes within the electrolyte layer.

Further, Fischer distinguishes primary and secondary inhibitors. Primary inhibitors are added to a composition in the active form, that is, these inhibitors' stoichiometric compositions do not change. Secondary inhibitors are generated at the interface during an electrode reaction. In practice, secondary inhibition is more prevalent.¹

According to Miksic and Miller³, "volatile corrosion inhibitors are secondary electrolyte layer inhibitors that possess appreciable saturated vapor pressure under atmospheric conditions, thus allowing vapor phase transport of the inhibitive substance." According to this definition, compounds that inhibit corrosion by only adjusting the pH of the electrolyte, e.g., volatile neutralizing amines, should not be necessarily called VCIs.

III. MECHANISM OF ACTION BY VCI

By definition, a vapor phase corrosion inhibitor must be a volatile compound or mixture of compounds. Additionally, a VCI must be capable of forming a relatively stable bond at the interface of the metal, thus producing a protective layer that limits penetration of the corroding species.^{9,10}

This mechanism is graphically illustrated in Figure 1, in which two functional groups are attached to the nucleus R: R*, which is responsible for the adsorption of the inhibitor on the metal's surface, and R**, which gives thickness and the impenetrable nature to the protective inhibitor layer.

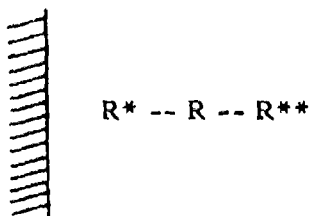


FIGURE 1. MECHANISM OF CORROSION INHIBITION
(After Miksic and Miller, 1980)

A VCI reaches the surfaces that it must protect from corrosion through the vapor phase. This transport mechanism requires the VCI to have an optimum vapor pressure. If the vapor pressure of the VCI is too low, e.g., on the order of 10^{-6} Torr at room temperature, the protective vapor concentration will be established only slowly. This action may result in insufficient corrosion protection during an initial time period. Further, if the space that houses both the stored equipment and the VCI is not sealed, sufficient inhibitor concentration may not be reached. Conversely, under similar conditions, if the vapor pressure of the VCI is too high (approximately 0.1 Torr at ambient conditions), its effectiveness will be limited to a short time period, as its consumption rate will be high. For these reasons, VCIs having "optimum" volatility are required for any given situation.

It is expected that under a given set of conditions, the rate of corrosion will rise as the temperature is elevated. Volatilization rate of VCIs may have a similar temperature dependence. For this reason, the available vapor phase concentration of a VCI may, in fact, self-adjust to the aggressiveness of the environment.^{1,10}

A more detailed mechanism describing the action of VCI is controversial. For example, it was shown by Rosenfeld¹¹ that the transport mechanism for di(cyclohexyl)amine nitrite involves vaporization of the inhibitor in a nondissociated molecular form, followed by hydrolysis on the surface of the metal. The products of hydrolysis may, then, provide for both cathodic and anodic inhibition.¹² Thus, in the case of this VCI, the protective group is formed on the surface to be protected. Baker, however, does not agree with this mechanism, but claims a dissociative transport mechanism instead.¹³

Rosenfeld¹¹ recorded the anodic and cathodic polarization curves of electrodes covered by a thin (circa 100 micrometers thick) electrolyte layer during his study of inhibitors at the metal-solution interface and their effect on the corrosion processes. In this work, he demonstrated that inhibition cannot be correlated to the alkalization process alone and that inhibition is usually due to the appropriate adsorbed organic cations on the metal's surface. Machu¹⁴ stated that reversible physical adsorption by van der Waals forces does not cause an effective interface inhibition compared with chemisorption which is not completely reversible.

IV. VAPOR PHASE CORROSION INHIBITORS

The efficiency of a compound as an inhibitor depends on its ability to be adsorbed on the metal's surface, the strength of this adsorption, and the temperature dependence of its vapor pressure. Each of these properties depends upon the chemical structure of the inhibitor.

Rosenfeld¹⁵ studied the effect of structure and the influence of substituents (OH, NO₂, NH₂) on the effectiveness of inhibitors. It was shown that for ferrous metals, aromatic nitrogen bases were ineffective corrosion inhibitors, even when additional hydroxyl or nitro groups were introduced. The majority of strong bases of aliphatic and alicyclic compounds were effective vapor-phase inhibitors. He found that cyclohexylamine (1)*, hexamethyleneimine (2), piperidine (3), morpholine (4), and benzylamine (5) were the most effective bases. It was claimed that the effectiveness of benzoates could be increased by the introduction of a highly

* Numbers in parentheses refer to chemical structures in Appendix A.

electrophilic nitro group into the ortho position or two nitro groups into the meta positions with respect to the carboxyl group. These groups reduce the electron density in the aromatic ring. Miksic¹⁶ claims that the nitro group-induced polarization shifts the steady-state potential of the metal in the positive direction, inhibiting the anodic reaction. Compounds that cause reduction of the nitro group will increase the oxidizing properties of the inhibitor. Complex ethers and weak aromatic amines were unsuitable inhibitors. Rosenfeld, et al.¹⁵ also evaluated several inorganic salts, and they found that ammonium carbonate $((\text{NH}_4)_2\text{CO}_3)$ and copper ammonium carbonate $(\text{Cu}(\text{NH}_3)_2\text{CO}_3)$ were effective inhibitors.

Trabanelli^{4,17} compiled a short table which listed the inhibiting efficiency values of various aliphatic, alicyclic, and aromatic amines, deduced from accelerated corrosion tests on Armco iron in the presence of 10 ppm of SO_2 . He concluded that "aliphatic and alicyclic compounds present inhibiting efficiencies superior to those of the aromatic substances having similar vapor pressures." His table from Reference 17 is reproduced here as Table 1.

Trabanelli¹⁷ in a further attempt to correlate the inhibitors' efficiency with their molecular characteristics came to the following expected conclusions: "the adsorption phenomenon...involves the availability of electrons on the atom or atoms considered as reaction centers for the formation of the metal-inhibitor bond. Naturally, the steric factors can also play a determining role on the inhibitor's action."

A general early dilemma of VCI research was that products that effectively prevented the atmospheric attack on ferrous materials did not behave similarly on nonferrous materials. Occasionally, these products even accelerated the corrosion process on the nonferrous materials, e.g., some amines attack copper and copper alloys due to the formation of soluble complexes.

Wakaoka and Yamamoto¹⁸ carried out corrosion tests on iron with various anions and organic acids. The degree of corrosion by anions decreased in the following

**TABLE 1. INHIBITING EFFICIENCIES OF DIFFERENT
ORGANIC SUBSTANCES, DEDUCED FROM ACCELERATED
ATMOSPHERIC CORROSION TESTS**
(Armco Iron in 10 ppm SO₂ Polluted Atmosphere)

Substances	% Inhibiting Efficiencies
None	--
n-hexylamine (6)	92
n-diethylamine (7)	57
n-octylamine (8)	94
n-decylamine (9)	84
n-dodecylamine (10)	50
cyclohexylamine (1)	80
dicyclohexylamine (11)	95
N,N-dimethylcyclohexylamine (12)	93
N,N-diethylcyclohexylamine (13)	94
aniline (14)	40
diphenylamine (15)	16
triphenylamine (16)	-17
N,N-dimethylaniline (17)	87
N,N-diethylaniline (18)	23
N,N-dimethyl-meta-toluidine (19)	52
N,N-dimethyl-para-toluidine (20)	80
N,N-diethyl-ortho-toluidine (21)	15
N,N-diethyl-meta-toluidine (22)	12
N,N-diethyl-para-toluidine (23)	44

order: thiosulfate, S₂O₃²⁻ > nitrate, NO₃⁻ > chloride, Cl⁻ > sulfate, SO₄²⁻ > dichromate, Cr₂O₇²⁻ > acetate, CH₃CO₂⁻ > cyanide, CN⁻ > orthophosphate, PO₄³⁻ > hydroxide, OH⁻ > carbonate, CO₃²⁻ > permanganate, MnO₄⁻ > iodide, I⁻ > ferricyanide, Fe(CN)₆³⁻ > ferrocyanide, Fe(CN)₆⁴⁻. The authors further stated that in case of corrosion by the fatty acid series, the degree of corrosion reached maximum where the carboxylic acids contained 8 to 10 carbon atoms.

Trabanelli⁴ also listed references that dealt with organic compounds for VCI purposes:

- primary (24), secondary (25), and tertiary (26) aliphatic amines^{13,19}
- aliphatic diamines (27)²⁰
- cycloaliphatic (28) and aromatic amines (29)¹⁷

- polymethylamines (30)²¹
- long-chain ethanolamines (31)²⁰
- imidazolines (32)^{19,20}
- amine salts of carbonic (33), carbamic (34), acetic (35), benzoic (36), oleic (37), nitrous (38), and chromic (39) acids^{11,19,20,22-32}
- acetylenic alcohols²²
- lauric alcohol (40)³³
- alkyl chromates (41)^{33,34}
- organic esters of nitrous acid (42)³³
- organic esters of phthalic acid (43)³³
- organic esters of carbonic acid (44)¹³
- nitronaphthalene (45)³⁵
- nitrobenzene (46)³⁶
- amides (47)¹³
- mixtures of nitrites with urea (48)³⁵, urotropine (49)³⁷ or ethanolamines (50)³⁷
- naphthols (51)³⁵
- thiourea (52) derivatives³⁸
- heterocyclic compounds, e.g., benzotriazole (53)^{39,40}
- nitrated (54) or sulfonated (55) petroleum derivatives^{41,42}
- organic acid derivatives⁴³⁻⁵¹

The first VCI suggested (British Patent No. 600328) was assigned to Shell in 1945. Some time ago, camphor was used to protect military materials made of ferrous metals. Naphthalene vapor was found to be an effective VCI for steel in an HCl-containing atmosphere at 250°-350°C. Cyclohexylamine, di(cyclohexyl)ammonium nitrite, and hexamethylenetetramine (49) were found to provide good protection of ferrous metals, but these compounds attack amphoteric nonferrous metals such as zinc and its alloys. Since most engines contain parts that are built of a variety of alloys, application of nitrite VCIs is limited. To overcome this difficulty, "mixed inhibitors" have been prepared. Since these products provide anodic and cathodic protection, they are effective not only for corrosion inhibition for ferrous metals but also for nonferrous metals. Inhibition of cathodic processes is accomplished by incorporating one or more oxidizing groups in the organic VCI compound.³ As Miksic and Miller claim, inorganic anions reduce only with difficulty on an iron cathode in a neutral electrolyte. It is further claimed that the cathodic process

rate can be accelerated by the introduction of an electrophilic substituent to reduce the electron density on the nitrogen. Carboxyl and nitro groups are strongly electrophilic substituents. These type of inhibitors are, however, weak in aggressive environments, e.g., those that contain chloride ions.

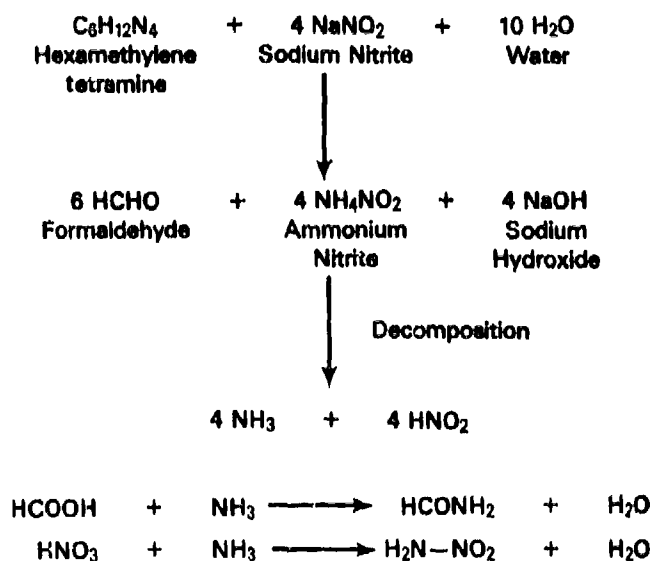
A relatively comprehensive recent review was written on VCI's by Singh and Banerjee.⁵² In this article, the authors categorized VCI's according to application to various metals, e.g., inhibitors for ferrous metals, for copper and copper alloys, for silver, for aluminum.

Protection of Ferrous Metals

Protection of ferrous metals may be accomplished by the application of amines and amine salts. Inhibiting efficiency of these compounds generally improves with increased molecular weight of the amine. Application of di(cyclohexyl)amine and its salt, e.g., its ammonium nitrite^{27,53} and other amines⁵⁴, have been discussed.

Studies of the kinetics of the electrochemical reactions on iron in a concentrated solution of sodium sulfate have shown that amino benzoates (56) affect iron only slightly. Amino nitrobenzoates (57) passivate iron mainly by an increase in the rate of the cathodic reduction reaction of the nitro groups. In the case of dilute electrolytes, nitrobenzoates also inhibit the anodic process.¹⁰

The most effective passivators for ferrous metals are claimed to be dinitro resorcinate (58) and sodium nitrophthalate (59), while dinitrobenzoate (60) and sodium dichromate (61) were found to have negligible effects.⁵⁵ Bum Sung Lee, et al.⁵⁶ studied the protective effects of hexamethylenetetramine (49) on iron, iron alloys, and aluminum in humid environments. They suggested that corrosion protection is based upon the following reactions:



Claims have been made in the Russian literature⁵⁷ that inclusion of a low-molecular weight surfactant substantially improves the VCI effectiveness, as it allows better wetting of the metal surface.

Some Russian workers⁵⁸ concluded that "inclusion of a nitro group, along with increasing surface area, facilitates passivation of the metal, which in turn improves protectivity."

Protection of Copper and Copper Alloys

Martin⁵⁹ and others^{11,22} showed that typical VCIs developed for the protection of ferrous metals in humid environments may cause corrosion of nonferrous metals due to the formation of soluble complexes. Representative examples of this compound class are cyclohexylamine carbonate (62), di(cyclohexyl)amine nitrite (63), and hexamethyleneimine benzoate (64). For the protection of brass, thiourea (52) derivatives, e.g., phenylthiourea (65), was recommended by Agarwal³⁸. While Barbior and Fland⁶⁰ observed that acetylenic alcohols inhibit atmospheric corrosion of copper, it was also shown by Fland²² that these same compounds accelerate the corrosion of iron. Tertiary-butanol chromate was shown to be a good inhibitor for zinc⁶¹ and other metals⁶².

A Japanese patent⁶³ claims that aqueous solutions of phenol carboxylic acids and esters, e.g., tannic acid (67), gallic acid (68), and water-soluble heterocyclic compounds, e.g., mercaptobenzothiazole (69), 2-aminobenzimidazole (70), provide for corrosion protection of copper even in aggressive storage environments. Benzotriazole (53) and tolyltriazole (71) have been reported to have excellent inhibiting effect on copper and copper alloys.^{64,65}

Gysling⁶⁶ reported that copper surfaces may be protected from the corrosive action of detergents and alkaline solutions by 2-guanidinobenzimidazole (72). A patent by Goulb and Sylvester⁶⁷ recommends the use of sodium mercaptobenzothiazole (73) for the protection of copper in the presence of soaps.

Protection of Silver

While silver is stable in reducing environments, it reacts in the presence of oxidizing agents and sulfur compounds. Japanese researchers⁶⁸ reported that benzotriazole (53) has an inhibiting effect on silver in a hydrogen sulfide atmosphere. It was suggested that the inhibitor forms a protective layer of silver complex on the surface of the metal.

Protection of Aluminum

Bum Sung Lee, et al.⁵⁶ prepared VCI papers, powders, and tablets from a mixture of hexamethylenetetramine (49) and sodium nitrite at a molar ratio of 1:4. Binders used with this system included milk casein and gum arabic. These researchers claim that the rust-inhibiting mechanism of this system is due partially to the fact that both of the ingredients are hygroscopic, and as they reduce moisture, they also reduce corrosion. More importantly, they decompose as they absorb water, and the decomposition products (as illustrated by the equations on page 12 of this draft), "formaldehyde and nitrous acid prevent surface corrosion of aluminum by the reducing action, and ammonia neutralizes acidic substances in the sealed atmosphere."

Protection of Ferrous and Nonferrous Metals

The following ten paragraphs are directly quoted from Reference 52, published in 1984. Reference numbers have been changed to agree with this report and the chemical structure numbers have also been added.

"In order to develop a universal inhibitor which may protect ferrous as well as nonferrous metals, enormous amount of work had been done all over the world and indeed many formulations have been suggested. Benzimidazole (74), 2-benzimidazolethiol (75), benzotriazole (53) and 2-mercaptobenzotriazole (76) are reported to be effective for Cu, Al, Zn and their alloys⁶⁹. Reaction products of methyl benzotriazole (77) with water soluble guanidine (78) class compounds such as guanidine carbonate or nitrate (79) or methyl (80), dimethyl (81), trimethyl (82), ethyl (83) or diethyl guanidine (84) in a molar ratio of 1:0.5-1:2 are effective atmospheric corrosion inhibitors for Cu, brass, Sn, tin plated steel and Al.⁷⁰ Products obtained by reaction of benzotriazole (53), ethylbenzotriazole and methyl benzotriazole (77) with soluble urea compounds, e.g., urea (48), methyl, ethyl, propyl or dimethyl urea (85) in a molar ratio of 1:0.5-1:2 at 10⁰-60°C are effective for Cu, steel, Al and Zn⁷¹.

"A compound formed by the reaction of 1 M benzotriazole, ethyl- or methyl-benzotriazole and 1-5 M amino compound of general formula $R_1R_2R_3N$ where R_1 and R_2 are hydrogen saturated or unsaturated C-18 hydrocarbon, phenyl, naphthyl or cycloalkyl and R_3 is hydrogen saturated or unsaturated C 1-11 hydrocarbon, is effective for Fe, Cu, Al, Zn and other metals⁷². The recommended amino compounds are methyl-morpholine (86), tridodecylamine (87), didodecylamine (88), dicyclohexylamine (11), and dimethyl aniline (89). The resultant inhibitor is soluble in machine, transformer, engine lubricating, and other mineral and vegetable oils.

"For protecting metals during storage, a compound formed by an incomplete reaction at 110°-170°C for 0.5-2 h of glycerine (90) or ethylene-glycol (91) with nitric acid and an alkanolamine with a primary or secondary alkylamine having more than six carbon atoms is used. The product is dissolved in a mineral oil. Mineral oil solution of salts of Zn, Mg or Pb in naphthenic acid together with 1-aminoethylimidazoline (92), is found suitable for temporary protection against atmospheric corrosion⁷³.

"The reaction product of benzotriazole (53) with polyamine, e.g., ethylene diamine (93) and carboxylic acid and dissolved in spindle oil, effectively resists atmospheric corrosion of Fe, Cu, Al, and Zn⁷⁴.

"Baligim, et al.⁷⁵ have reported protective properties of mixtures of benzotriazole with benzoates of ammonia (94), guanidine (95), hexamethylene-diamine (96) and monoethanolamine (97) in relation to steel, Cu, Zn, and Cd. The mixtures showed a synergistic protective action in case of steel, Zn and Cd. Mixture of benzotriazole (53) with guanidine benzoate (95) and ammonium benzoate (94) afforded the best protection. Solidified products of cyclohexylamine (1), di(cyclohexyl)amine (11), propylamine (98) and butylamines (99) with a concentrated solution of benzylidene sorbite (100) in organic acid are reported to have good protecting properties towards ferrous and nonferrous metals. Also, 3,5-diphenyl (101) or 3,5-bis-(R-phenyl)-2,2,4-triazole (102), where R is hydrogen, alkyl or hydroxyl, is reported to protect gaseous or aqueous attack on Cu, Ag, Fe, Al, Ni, and their alloys⁷⁶.

"Quarternary ammonium salts (namely tetrabutyl, tetramethyl) of valeric (103), caprylic (104), capric (105), butyric (106), lauric (107), myristic (108), tridecylic (109), palmitic (110), stearic (111), benzoic (36) and carbamic acids (34) and also *o*-, and *p*-nitrophenates (112) are effective for steel, Cu and brass.⁷⁷ In another study, tetrabutyl ammonium *o*-nitro phenate (113) was found most effective for steel and have no effect on Cu and brass⁷⁸.

"In atmospheres polluted with SO_2 and H_2S 4-H-1,2,4-triazole (114) or its derivatives in combination with known inhibitors such as di(cyclo-octyl)amine nitrite (115), urea, NaNO_2 , etc., is effective for Fe, Al, steel, Cu, Ag, Zn, Ni, Sn, Cd, Mg, Pb, and their alloys⁷⁹. A Dutch patent⁸⁰ describes the solution of an aromatic hydrocarbon, an alkyl metal nitrate and alkyl-substituted benzotriazole impregnated in paper, to be effective for metal articles made of Al, Zn, Cu, steel, and other metals and alloys.

"Substituted pyrazoles (116) dissolved in water, methanol or ethanol and impregnated in paper offer protection more effectively than di(cyclo-hexyl)amine (11) nitrite towards atmospheric attack on Al, Cu, Zn, Sn, and other nonferrous metals.⁸¹ Anan, et al.⁸² have tested a number of wood industry products as vapour phase inhibitors and have reported that 2,5-dimethylfuran (117) is an excellent inhibitor for nonferrous metal. Cast iron, steel, copper, brass, aluminum solder and other metals may be protected by reaction product of 1 mole of cinnamic acid (118) with 1-1.05 mole amine (diethylamine (119), triethylamine (120), diethanolamine (121), cyclohexylamine (1) etc.) with or without solvent, e.g., water⁸³. An adduct of 4 or 5 halohydroxy and/or nitrosubstituted benzotriazole with a primary, secondary or tertiary amine is reported to be a highly effective inhibitor for Al, cast iron, steel, brass, solder, copper and other metals and alloys.⁸⁴

"A mixture of benzotriazole with substances of oxidative character, e.g., nitromethane (122), nitronaphthalene (123), dinitrophenol (124), m-nitrobenzoic acid (125) dissolved in acetone or dimethyl phthalate (126) provided good protection towards steel, grey cast iron, Cu, brass, galvanised iron, and Pb in humid atmosphere⁸⁵. A ternary mixture comprising of benzotriazole (53) and sodium carbonate, mixed with urotropine (49) is highly effective towards steel and Cu⁸⁶. A composition containing by parts 3-30 of benzotriazole (53) and higher aliphatic amine (octadecylamine) (127) ensures protection of ferrous metals, Cu

and Cu alloys, Al and Al alloys, Zn, Cd, Pb Ni and Cr and phosphate and oxide coatings⁸⁷.

In a long exposure test conducted for six years in humid atmosphere by Komrova⁸⁸ on steel, Cu, brass and galvanised iron using dibutylphthalate (128), isoamylcinnamate (129), triamylborate (130), or the nitrobenzoate (131) and other esters, it was concluded that these esters (apart from dibutylphthalate) provide complete corrosion protection towards steel, Cu and brass at relative humidity values up to 98% and of galvanised iron at relative humidity values up to 85%⁸⁸. Besides the above formulations discussed for ferrous and nonferrous metals, a number of other patents are also available in the literature but provide very little information about their exact nature⁸⁹⁻¹¹²."

Lea¹¹³ studied the inhibition of oxidation of Fe-10% Cr steel at 600°C in air contaminated with vapor phase boron from B₂O₃. Using Auger electron spectroscopy (AES), he found that the boron is concentrated in the surface 10-20 nm layer. The presence of boron resulted in the enrichment of the free surface with chromium oxide, instead of the iron oxide that is found there in the absence of boron. It was concluded that the boron prevents the ingress of oxygen into the oxide film by the introduction of networks of -O-B-O- covalent bonds in the oxide structure.

Hendy and coworkers¹¹⁴ also studied the effect of borates on the oxidation of iron-chromium alloys. They observed that boric acid (132) will dehydrate in an oven held at 300°-600°C. This dehydration is accompanied by "considerable volatilization." When an iron-chromium alloy is introduced into the furnace, boron oxide (B₂O₃) will deposit on the metal's surface, which will inhibit oxidation in air for several thousand hours at 600°C, even if the specimens are transferred to a furnace without boron source.

Sanyal and Gupta¹¹⁵ studied the effect of several VCIs against the following fungi: aspergillus japonicus, curvularia lunata, penicillium pinophilum, trichoderma sp., and cladosporium sp. They found that meta-dinitrobenzene (133) completely inhibited fungal growth, sporulation, and pigmentation of each of the test fungi.

V. EVALUATION OF VCIs

Romanov and Khanovich¹¹⁶ claim that the effectiveness of VCIs may be evaluated in terms of the following parameters:

- time of inhibitor loss;
- relative loss of inhibitor;
- time of appearance of first corrosion products;
- relative residual quantity of inhibitor when corrosion starts;
- rate of corrosion;
- factor which allow for the nature of corrosion.

Measurement of vapor pressure is important in developing a VCI for the various systems. One method to measure vapor pressure is claimed to involve the determination of diffusion rate of gases through a small orifice. The rate of effusion is determined by measuring the shrinkage of a highly sensitive quartz spring by using a cathetometer. Martin⁵⁹ determined the saturated vapor pressure, and its dependence on temperature of various VCIs by an effusion method.

Various accelerated corrosion tests are in use. Before using any of these tests, one must exercise caution³ as experimental results of accelerated tests in which artificially increased concentrations of corrosive agents, e.g., SO_2 , H_2S , or NaCl , are used, should be compared to actual field performance only after proper calibrations. This warning was also expressed by Rosenfeld¹¹⁷, explaining that "reproducibility of data depends upon experimental parameters that are inherent properties of the test method employed."

A widely used evaluating method to describe the relative abilities of inhibitors to prevent rusting of steel is described under ASTM D 1748, entitled "Rust Protection by Metal Preservatives in the Humidity Cabinet." The summary of this method is stated as "steel panels are prepared to a prescribed surface finish, dipped in the test oil, allowed to drain and then suspended in a humidity cabinet at $48.90 \pm 1.1^\circ\text{C}$

($120^{\circ} \pm 20^{\circ}\text{F}$) for a specified number of hours. The oil fails or passes the test according to the size and number of rust dots on the test surfaces of the panels." An essentially identical test method is described under Federal Test Method Standard No. 791B, Method 5329.1, entitled "Corrosion Protection (Humidity Cabinet)."

Lea¹¹³ used Auger electron spectroscopy (AES) to detect and determine the depth distribution of trace quantities of boron in the surface layer of an iron-chromium steel. Such a technique can obviously be expanded to many other inhibitor systems. The use of another analytical method, "Electron Spectroscopy for Chemical Analysis," ESCA, with its unique capabilities for surface analysis also offers promise for these investigations. (ESCA probes only the top $30\text{--}50\text{\AA}$ of a surface, but it provides both elemental analysis and chemical bonding information. It is also a nondestructive method that analyzes any solid surface. It is sensitive to all elements except hydrogen).

A number of other methods have also been used for the investigation and evaluation of VCIs. Measurement of the quantity of inhibitor adsorbed on the metals' surface may be accomplished by the use of a sufficiently sensitive microbalance.^{33,118} Rosenfeld¹¹⁹ followed the degree of VCI-provided protection of metal specimen by measurement of changes in their ohmic resistance. Kar¹²⁰ used capacitance measurements in kinetic studies of the electric double layer on the metals' surface. Electrochemical methods for the investigation of VCIs have been used by Shekhter⁴¹, Trabanelli¹⁷, Rosenfeld¹¹, and others.^{24,42,121,122}

Autoradiography was used by Rosenfeld¹² and Hendricksen¹²³ for the determination of surface distribution of VCIs. Hendricksen¹²³ also showed that when metal surfaces were exposed to VCIs in closed containers, they were covered by a hydrophobic adsorbed layer. He measured the contact angle of distilled water on these surfaces.

Schwabe^{53,121} and others¹²⁴ used radiochemical methods to evaluate ^{14}C -containing di(cyclohexyl)amine (11) and its nitrite, as well as dibenzyl sulfoxide (134). Rosenfeld¹²⁵ and Poling¹²⁶ used infrared techniques to study VCI deposits. Yu Yao¹²⁷ used mass spectroscopy to study the effects of various amines as corrosion inhibitors on iron surfaces.

VI. APPLICATIONS

Recommendations for given formulations and applications may vary not only according to the composition of the specific equipment to be protected, but also according to the expected storage conditions. The various storage conditions that require progressively more aggressive treatments are: (a) enclosed nonventilated areas, (b) uncovered inside storage, (c) sheltered outside storage, and (d) uncovered outside storage.

The VCIs may be either oil- or water-soluble type. Normally VCIs are dispensed as powders, cakes, sprays, and impregnated papers and foams. Deposition of some water-soluble additives, e.g., sodium nitrite, may be accomplished by dipping in, or spraying an aqueous or aqueous glycerol solution of the substrate, followed by drying. Such a technique has been used for passivation of ferrous metals.¹²⁸

Similarly, protection of copper alloys was accomplished by dipping them in a warm, aqueous solution of benzotriazole.¹²⁹

Normally the application techniques for VCIs consist of depositing the inhibitor from an alcoholic solution, aspiration of inhibitor-saturated air across the object to be protected, or wrapping the metals in inhibitor-treated paper. Treatment with vapor phase corrosion inhibitors naturally also permits the protection of internal engine parts from corrosion.¹³⁰ Trabenelli⁴, while recommending the use of 2-methylpiperazine for the protection of turbines, cautions that simultaneous use of desiccants, e.g., silica gel, must be avoided, as these products may adsorb the VCIs, thereby reducing their effectiveness. Others¹¹⁹, however, use silica gel as the carrier for VCIs.

A summary of the various VCI compound classes recommended for the protection of several alloys is presented in Table 2.

In present practice, most engine manufacturers give specific recommendations for preservation procedures. A summary of these various procedures and recommendations, as compiled by Radian Inc. for the U.S. Army Materials, Fuels, and Lubricants Laboratory¹³², Ft. Belvoir, VA, is presented in Appendix B.

TABLE 2. PROTECTION OF VARIOUS ALLOYS BY CORROSION INHIBITORS

Compound Class	Alloys of				
	Iron	Copper	Silver	Aluminum	Zinc
Naphthalene	+	ND	ND	+	ND
Ammonia	+	-	ND	ND	ND
Alkyl amines	+	-	ND	+	ND
Alkyl amine salts	+	ND	ND	ND	ND
Cyclo-aliphatic amines	+	-	ND	ND	ND
Dicyclo-aliphatic amines	+	-	ND	+	ND
Dicyclo-aliphatic amine salts	+	+	ND	+	ND
Aromatic amines	+	-	ND	-	ND
Nitroaromatic acids	+	-	ND	ND	ND
Aminol salts	+	ND	ND	+	ND
Aminol with surfactant	+	ND	ND	ND	ND
Silicone amines	ND	- to +	ND	ND	ND
Acetylenic alcohols	ND	+	ND	ND	ND
Phenol carboxylic acids and esters	ND	+	ND	ND	ND
Fatty acid quart. amm. salts	+	+	ND	ND	ND
Urea	+	ND	ND	ND	ND
Thiourea	ND	+	ND	ND	ND
Thiazoles	+	+	+	+	+
Benzimidazole	+	+	+	+	+
Benzotriazoles	ND	+	+	ND	ND
Benzotriazoles and tert. amines	+	+	ND	+	+
Benzotriazoles and polyamine	+	+	ND	+	+
Benzotriazole + di-(cyclo-octyl)amine nitrite	+	+	+	+	+
<hr/>					
+	Effective				
-	Deleterious				
ND	No data				

Sources: Ref. 52 and 131

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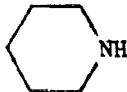
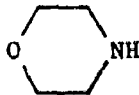
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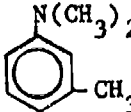
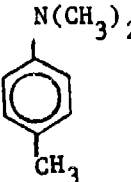
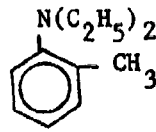
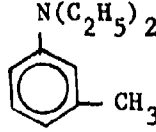
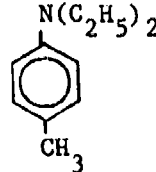
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APPENDIX A


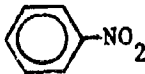
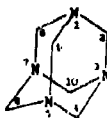

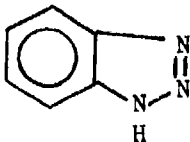
IDENTIFICATION OF COMPOUNDS

APPENDIX A
IDENTIFICATION OF COMPOUNDS

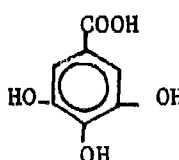
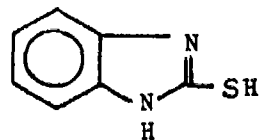
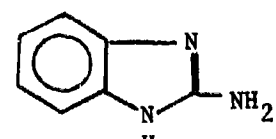
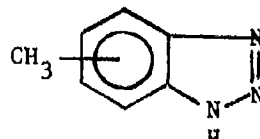
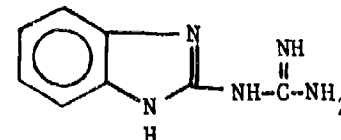
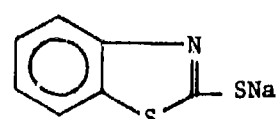
Structure Number	Name	Structure
1	Cyclohexylamine	$C_6H_{11}-NH_2$
2	Hexamethyleneimine	
3	Piperidine	
4	Morpholine	
5	Benzylamine	$C_6H_5CH_2NH_2$
6	Hexylamine	$CH_3(CH_2)_5NH_2$
7	Diethylamine	$[CH_3(CH_2)_5]_2NH$
8	Octylamine	$CH_3(CH_2)_7NH_2$
9	Decylamine	$CH_3(CH_2)_9NH_2$
10	Dodecylamine	$CH_3(CH_2)_{11}NH_2$
11	Di(cyclohexyl)amine	$(C_6H_{11})_2NH$
12	<u>N,N</u> -Dimethylcyclohexylamine	$C_6H_{11}-N(CH_3)_2$
13	<u>N,N</u> -Diethylcyclohexylamine	$C_6H_{11}-N(C_2H_5)_2$
14	Aniline	$C_6H_5-NH_2$
15	Diphenylamine	$(C_6H_5)_2NH$

Structure Number	Name	Structure
16	Triphenylamine	$(C_6H_5)_3N$
17	<u>N,N</u> -Dimethylaniline	$C_6H_5-N(CH_3)_2$
18	<u>N,N</u> -Diethylaniline	$C_6H_5-N(C_2H_5)_2$
19	<u>N,N</u> -Dimethyl- <u>m</u> -Toluidine	
20	<u>N,N</u> -Dimethyl- <u>p</u> -Toluidine	
21	<u>N,N</u> -Diethyl- <u>o</u> -Toluidine	
22	<u>N,N</u> -Dimethyl- <u>m</u> -Toluidine	
23	<u>N,N</u> -Diethyl- <u>p</u> -Toluidine	
24	Primary Aliphatic Amine	$R-NH_2$
25	Secondary Aliphatic Amine	$RR'NH$
26	Tertiary Aliphatic Amine	$RR'R''N$

Structure Number	Name	Structure
27	Aliphatic Diamine	
28	Cycloaliphatic Amine	
29	Aromatic Amine	
30	Polymethyl Imine	See No. 28
31	<u>N</u> -Substituted Ethanol Amine	$\text{HO-CH}_2\text{CH}_2\text{-NR}_2$
32	Imidazolines (Dihydro Imidazoles)	
33	Carbonic Acid	H_2CO_3
34	Carbamic Acid	$\text{H}_2\text{N-COOH}$
35	Acetic Acid	$\text{CH}_3\text{-COOH}$
36	Benzoic Acid	$\text{C}_6\text{H}_5\text{-COOH}$
37	Oleic Acid	$\text{CH}_3(\text{CH}_2)_7\text{CH=CH}(\text{CH}_2)_7\text{COOH}$
38	Nitrous Acid	HNO_2
39	Chromic Acid	H_2CrO_4
40	Lauric Alcohol	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OH}$
41	An Alkyl Chromate	R_2CrO_4
42	An Organic Ester of HNO_2	RONO
43	Diester of Terephthalic Acid	

Structure Number	Name	Structure
44	Diester of Carbonic Acid	$(RO)_2CO$
45	2-Nitronaphthalene	
46	Nitrobenzene	
47	Amide Group	$\begin{array}{c} \diagup \\ -C-N \\ \parallel \quad \diagdown \\ O \end{array}$
48	Urea	$\begin{array}{c} H_2N-C-NH_2 \\ \parallel \\ O \end{array}$
49	Urotropine or Methenamine or Hexamethylenetetramine	
50	An Ethanolamine	$HO-CH_2CH_2-N \begin{array}{l} \diagup R \\ \diagdown R' \end{array}$
51	2-Naphthol	
52	Thiourea	$\begin{array}{c} S \\ \parallel \\ H_2N-C-NH_2 \end{array}$
53	Benzotriazole	
54	Nitrated Petroleum Derivative	$-C-ONO_2$

Structure Number	Name	Structure
55	Sulfonated Petroleum Derivative	$-C-OSO_3H$
56	An Amino Benzoate	$RNH_3^+ \cdot OOC-C_6H_5^-$
57	An Amino Nitrobenzoate	$RNH_3^+ \cdot OOC-C_6H_4(NO_2)^-$
58	A Dinitro Resorcinate	$O=C_6H_3(NO_2)_2O^-$
59	A Sodium Nitrophthalate	$O_2N-C_6H_4-COO^- Na^+ \cdot COOH$
60	A Dinitrobenzoate	$COO^- -C_6H_3(NO_2)_2$
61	Sodium Dichromate	$Na_2Cr_2O_7$
62	Cyclohexylamine Carbonate	$[C_6H_{11}-NH_3^+]_2CO_3^{2-}$
63	Di(cyclohexyl)amine Nitrite	$[(C_6H_{11})_2NH_2^+]ONO^-$
64	Hexamethyleneimine Benzoate	$C_6H_{11}N^+ \cdot OOC-C_6H_5^-$

Structure Number	Name	Structure
65	Phenylthiourea	$\text{H}_2\text{N}-\overset{\overset{\text{S}}{\parallel}}{\text{C}}-\text{NH}-\text{C}_6\text{H}_5$
66	<u>t</u> -Butanol Chromate	$(\text{CH}_3)_3\text{COCrO}_4\text{H}$
67	Tannic Acid	Approx. $\text{C}_{76}\text{H}_{52}\text{O}_{18}$
68	Gallic Acid	
69	2-Mercaptobenzothiazole	
70	2-Aminobenzimidazole	
71	"Tolyltriazole"	
72	2-Guanidinobenzimidazole	
73	Sodium Mercaptobenzothiazole	

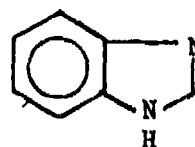
Structure
Number

Name

Structure

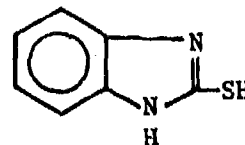
74

Benzimidazole



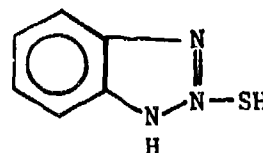
75

2-Benzimidazolethiol



76

2-Mercaptobenzotriazole



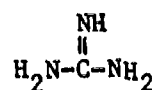
77

Methyl Benzotriazole

See No. 71

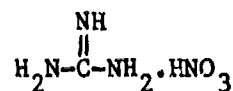
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Guanidine



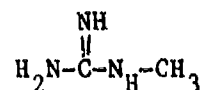
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Guanidine Nitrate



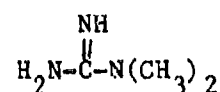
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Methyl Guanidine

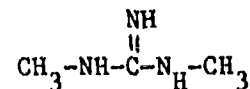


81

Dimethyl Guanidine

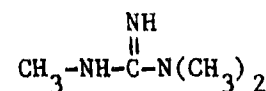


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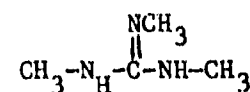


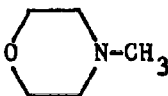
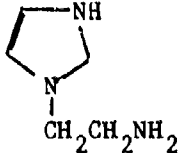
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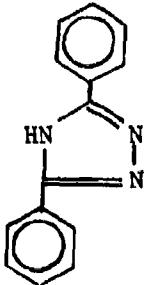
Trimethylguanidine

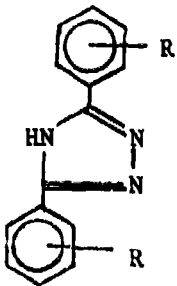



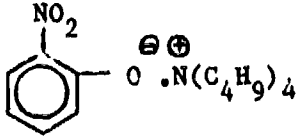

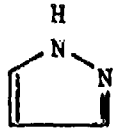
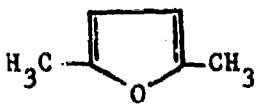

OR



Structure Number	Name	Structure
83	Ethylguanidine	$\begin{array}{c} \text{NH} \\ \\ \text{H}_2\text{N}-\text{C}-\text{NHC}_2\text{H}_5 \end{array}$
84	Diethylguanidine	$\begin{array}{c} \text{NH} \\ \\ \text{H}_2\text{N}-\text{C}-\text{N}(\text{C}_2\text{H}_5)_2 \end{array}$
85	Dimethyl Urea	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3-\text{NH}-\text{C}-\text{NH}-\text{CH}_3 \end{array}$ <p>OR</p> $\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{N}-\text{C}-\text{N}(\text{CH}_3)_2 \end{array}$
86	<u>N</u> -Methylmorpholine	
87	Tri(dodecyl)amine	$(\text{C}_{12}\text{H}_{23})_3\text{N}$
88	Di(dodecyl)amine	$(\text{C}_{12}\text{H}_{23})_2\text{NH}$
89	<u>N,N</u> -Dimethyl Aniline	$\text{C}_6\text{H}_5-\text{N}(\text{CH}_3)_2$
90	Glycerine or Glycerol	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CH}\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$
91	Ethylene Glycol	$\text{HOCH}_2\text{CH}_2\text{OH}$
92	1-Aminoethylimidazoline	

Structure Number	Name	Structure
93	Ethylene Diamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$
94	Ammonium Benzoate	$\text{C}_6\text{H}_5\text{COOH} \cdot \text{NH}_3$
95	Guanidine Benzoate	$\begin{array}{c} \text{NH} \\ \\ \text{H}_2\text{N}-\text{C}-\text{NH}_2 \cdot \text{HOCC}_6\text{H}_5 \end{array}$
96	Hexamethylene Diamine Benzoate	$\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2 \cdot \text{HOCC}_6\text{H}_5$
97	Monoethanolamine Benzoate	$\text{HOCH}_2\text{CH}_2\text{NH}_2 \cdot \text{HOCC}_6\text{H}_5$
98	Propylamine	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$
99	Butylamine	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
100	Benzylidene Sorbite	$\begin{array}{c} \text{CH}=\text{CH}-\text{C}_6\text{H}_5 \\ \\ \text{CHOH} \\ \\ \text{CHOH} \\ \\ \text{CHOH} \\ \\ \text{CHOH} \\ \\ \text{CH}_2\text{OH} \end{array}$
101	3,5-Diphenyl-1,2,4-Triazole	

Structure Number	Name	Structure
102	3,5-bis-(R-Phenyl)-1,2,4-Triazole	
103	Valeric Acid	$\text{CH}_3(\text{CH}_2)_3\text{COOH}$
104	Caprylic Acid	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$
105	Capric Acid	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$
106	Butyric Acid	$\text{CH}_3(\text{CH}_2)_2\text{COOH}$
107	Lauric Acid	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$
108	Myristic Acid	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$
109	Tridecylic Acid	$\text{CH}_3(\text{CH}_2)_{11}\text{COOH}$
110	Palmitic Acid	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
111	Stearic Acid	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
112	p-Nitrophenate	

Structure Number	Name	Structure
113	Tetrabutyl Ammonium <u>o</u> -Nitrophenate	
114	4-H-1,2,4-Triazole	
115	Dicyclooctylamine Nitrite	$(C_8H_{15})_2NH.HNO_2$
116	Pyrazole	
117	2,5-Dimethylfuran	
118	Cinnamic Acid	$C_6H_5-CH=CH-COOH$
119	Diethylamine	$(C_2H_5)_2NH$
120	Triethylamine	$(C_2H_5)_3N$
121	Diethanol Amine	$(HOCH_2CH_2)_2NH$
122	Nitromethane	CH_3NO_2
123	1-Nitronaphthalene	

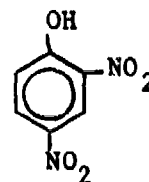
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Name

Structure

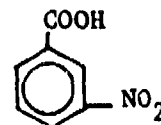
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2,4-Dinitrophenol



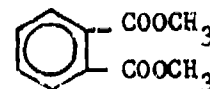
125

m-Nitrobenzoic Acid



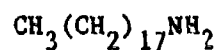
126

Dimethylphthalate



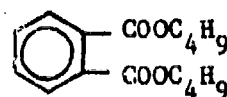
127

Octadecyl Amine



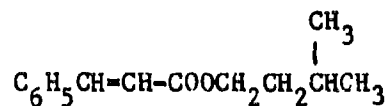
128

Dibutylphthalate



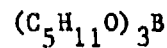
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Isoamylcinnamate



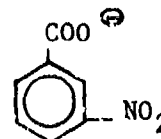
130

Triamylborate



131

A Nitrobenzoate



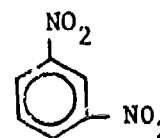
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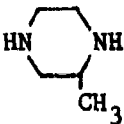
Boric Acid



133

m-Dinitrobenzene



Structure Number	Name	Structure
134	Dibenzyl Sulfoxide	$\text{C}_6\text{H}_5-\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{S}}}-\text{CH}_2-\text{C}_6\text{H}_5$
135	2-Methylpiperazine	

APPENDIX B

SUMMARY OF COMMERCIAL PRESERVATION PROCEDURES

(Excerpted from "Engine Preservation Procedures,"
Reference 132 of this report)

SUMMARY OF COMMERCIAL PRESERVATION PROCEDURES

This section summarizes the preservation procedures used by the manufacturers contacted during the course of the study. The detailed procedures are in either Appendix B, Engine Preservation Procedures, or in Appendix F, Telecons.

- **Alco Power:** Alco engines are preserved beginning with hot testing the engine on a test stand while using a preservative lubricating oil in the engine lubrication system. Near the end of the hot test the fuel system is flushed with P-10 preservative. When the engine is turned off the last injected quantity of P-10 preserves the combustion chambers. This provides preservation for in excess of 1 year.
- **Bombardier:** This company referred us to their U.S. Representatives, Alco Power.
- **Briggs & Stratton/Lombardini diesel:** "Treat" lubrication and injection systems and all moving parts with MIL-L-21260 specification anti-rust oil, by turning engine and discharging excess anti-rust oil. This also entails removal of injectors to "Treat" the combustion chamber.
- **Caterpillar - Engines:** Add Volatile Corrosion Inhibitor (VCI) oil to clean crankcase oil at rate of three to four percent by volume. Crank engine and spray a 50/50 mixture of engine oil and VCI oil into air or turbo inlet. Spray same mixture through exhaust valves. Seal air and exhaust openings. Spray 50/50 mixture of engine oil and VCI oil into cylinder through injector ports. Bar engine over slowly to put oil on cylinder walls. Preservation provides protection for 1 year of storage.
- **Colt Pielstick (Fairbanks-Morse):** All military engines preserved per contract obligations. They recommend military preservation specification procedures for domestic engines destined for long-term storage.
- **Cooper Energy Services - Superior Engines**
 - Domestic shipment and/or storage, 1 year minimum protection: Performance testing will be performed while using rust preventing lubricating oil. Spray rust preventing oil inside each cylinder and on all exposed surfaces inside the crankcase. Seal all openings and cover unit with heavy waterproof tarp for outdoor storage and transportation.
 - Export Shipment or Hazardous Storage: As above, except also pump a 50/50 mixture of rust preventing oil and diesel fuel through fuel system, and instead of covering engine with tarp the engine should be boxed in a waterproof box.
- **Cummins Engine Co:** All military engines are preserved per contract obligations. Commercial engines to be stored more than 6 months are required to use a rust inhibiting engine oil in the engine during the engine performance test. Stored engines are to be visually inspected and represerved annually.

- Deutz Engines: Preserve to Level A of MIL-E-10062E(2).
- Ford Motor Company, Industrial Engines Operations: Change engine oil using recommended oil. Run engine out of diesel fuel, then restart and run for 10 minutes on engine oil stabilized diesel fuel. At completion of run, spray recommended engine oil into air intake for 2 minutes. Open throttle for short burst of speed, shut off, and continue spraying oil into air intake until engine stops. Seal all openings.
- General Motors - Detroit Diesel: Fill crankcase with MIL-L-21260. Fill fuel tank with 10 minute supply of anti-rust fuel oil. Operate engine for five minutes. Engine preserved for storage in excess of 30 days.
- General Motors Electromotive Division: Remove oil pan hand hole covers and valve rocker/top deck covers, and inspect the oil pan and valve rocker gear, fuel supply components, and top deck area for carbon-type deposits. Any visible deposits should be sprayed with diesel fuel to break up the deposit. Replace covers and fill fuel tank with sufficient quantity of quality fuel to run engine on idle for a 15-minute period. Drain crankcase and refill with rust prevention oil. Run the engine for a 15-minute period. Drain fuel system and purge with rust preventing oil. Remove air box hand hole covers. Spray air box and each cylinder liner bore with rust preventing oil through the air intake ports when the ports are uncovered by barring the engine over. Replace air box hand hole covers. Remove oil pan hand hole covers. Spray lower end of cylinder liners with rust preventing oil. Replace oil pan hand hole covers. Remove valve rocker/top deck covers and spray all parts with rust preventing oil. This preservation provides protection for 2 years of storage.
- Hatz: Fill engine with preservation oil. Add preservation oil to fuel in ratio of one part oil to four parts fuel (1:4). Run the engine 10 to 15 minutes. Seal air inlet and exhaust outlet. Preservation provides protection for 2 years of storage.
- Hawker Siddeley Lister Diesel: Engines are run at factory which provides protection for shipment and storage for less than 1 year.
- International Harvester: Drain fuel tank, refill with 12 gallons of approved diesel fuel. Add 2 oz. fuel stabilize and 1.5 oz. VCI oil to fuel. Run engine at 1400-1600 rpm for 4 minutes. Change oil, adding 0.5 oz. VCI oil for each quart of engine lube oil capacity. Run engine at 1400-1600 rpm for 30 seconds. Pour 4 oz. VCI oil into intake manifold. Seal air inlet, exhaust outlet, crankcase breather, and fuel tank vent line. Preservation provides protection for 6 months of storage.
- Perkins Engines: Change engine oil using approved grade. Drain fuel tank, fill with one gallon of specified oil. Run engine approximately 15 minutes at half maximum speed. Drain cooling system. Remove injectors and pour castor oil into cylinder. Replace injectors and slowly bar the engine one complete revolution. Seal air inlet and exhaust manifold.

- Ransome Engine: All engines are filled with normal operating oil, all openings plugged and sealed, water jackets emptied, and stored under plastic tarp. Preservation provides protection for 1 year of storage.
- Republic Engine Corp: Republic diesel engines are coated in cosmoline and crated for shipment to America from China.
- Teledyne Continental Motor: All engines are preserved per Level A of MIL-C-10062E(2).
- Teledyne Wisconsin Motor: All military contract engines are preserved by a subcontractor to contract obligations. Non-military engines are fogged off with engine oil at the completion of the performance test. The engine openings are sealed and rust preventing oil is applied to all bare metal surfaces.
- Transamerica Delaval: Their internal specification for preservation is similar in scope to MIL-E-1006E(2). They use a mixture of VCI and rust preventative oil to preserve engines.
- Volkswagon: Operate engine until warm. Drain the engine oil and refill with preservative oil. Run engine at fast idle for 30 seconds. With the engine running, slowly pour an amount of preservative oil into the carburetor/air intakes. Stop the engine. Remove the spark plugs/injectors and squirt preservative oil into the combustion chambers. Crank the engine and replace spark plugs/injectors.
- Waukesha Engine Division, Dresser Industries: Change the engine oil and operate engine long enough to fully circulate the fresh engine oil. Add appropriate amounts of Waukesha preservative oil, which is engine oil with volatile corrosion inhibitors added to the oil pan, oil bath air filters, fuel tanks, and multi-plunger injection pumps. Connect fuel supply line to a source of a mixture of preservative oil and fuel oil. Crank engine for 20 seconds and remove injectors. Add preservative oil to each cylinder and replace injectors. If storing for more than 1 year, inspect and represerve annually, as necessary.
- J. H. Westerbeke Corp: Military contract engines are preserved per contract obligations. Non-military engines are not preserved.
- White/Hercules Engines: Remove injectors and squirt slushing oil or clean, heated crankcase oil into each cylinder. Fill crankcase with anti-rust engine oil. Turn engine over slowly to distribute oil in cylinders. Note: Apparently all engines are preserved at factory per Level A, MIL-E-10062E(2).
- Yanmar Diesel Engines: Yanmar engines are packaged in crates, which are shipped to America in sealed containers. The engines are not preserved internally.

CATEGORIZATION OF COMMERCIAL PRESERVATION PROCEDURES

A survey of commercial manufacturers was made to determine what preservation procedures are being used. A list of over 40 diesel engine manufacturers was compiled. Procedures were received from 23 manufacturers and 2 oil companies. These responses can be broken into five basic procedures for preserving engines. These are listed below, along with the manufacturers who use them. Each type of procedures will be explained in detail under the SUMMARY OF CANDIDATE Preservation Procedures Section to be found on page III-4 (page 58 of this Appendix).

A. MIL-C-10062E(2): This procedure or variations of it is the most prevalent, particularly among the manufacturers whose products are very large and expensive. Others who use it do so because of Military Contract Obligations. It or its variations are used by:

- Colt Pielstick (Fairbanks-Morse)
- Cooper Energy Services - Superior Engines
- Cummins (only used for Military Contract Engines)
- Deutz (only used for Military Contract Engines)
- Electromotive Division, G.M.
- Onan (only used for Military Contract Engines)
- Teledyne Continental Motors
- Teledyne Wisconsin Motors (only used for Military Contract Engines)
- Transamerica Delaval, Engine & Compressor Division
- J. H. Westerbeke Corp. (only used for Military Contract Engines)

B. Use preservative fuel in fuel system, or add preservative additive to fuel. Change crankcase oil, using fresh preservative lubricating oil or preservative additive in fresh normal lubricating oil. Run engine for 10 to 15 minutes or until preservative fuel is flowing from removed injector fuel return line. Seal air inlets and exhaust.

- Alco Power
- Cummins
- Detroit Diesel Allison
- Deutz
- Hatz
- Hawker Siddeley Lister
- International Harvester

C. Preserve engine per procedure B above, and in addition, once the engine shuts off remove the fuel injectors and spray preservative oil into the cylinders. Turn engine over one revolution to spread preservative oil over the cylinder walls, and reinstall fuel injectors.

- Briggs & Stratton/Lombardini
- Caterpillar
- Cooper
- Electromotive Division, G.M.
- Perkins Engine Company
- Volkswagon
- Waukesha Engine
- White/Hercules Engine

D. Preserve the engine per procedure B above, and in addition, fog or spray engine oil/preservative oil through air intakes, beginning 2 minutes prior to shutoff. After engine shutoff, turn off oil spray.

- Ford Motor Company, Industrial Engines Operation
- Mobil Oil Company
- Teledyne Wisconsin Motors

E. No specific preservation procedure for protecting internal components during storage/shipment.

- Amoco (Operate engine every 3 months)
- Isuzu
- Onan
- Ransome Engines
- Republic Engine Company
- J. H. Westerbeke Company
- Yanmar of America

SUMMARY OF CANDIDATE PRESERVATION PROCEDURES

The following is a detailed listing of the five candidate preservation procedures. Candidate Procedure A is comparable to the MIL-E-10062 procedure. Candidate Procedures B, C, D, and E were obtained from a compilation of procedures used by commercial engine manufacturers. Candidate Procedure E is unique because it does not make an effort to provide for combustion chamber preservation. These procedures have been written in the style of the military specification for ease of comparison.

CANDIDATE PROCEDURE "A"

New equipment shall have engine crankcases drained of existing lubricating oil. The drain plug shall be replaced. The engine crankcase shall be filled to the operating level with the correct grade (weight) of preservative lubricating oil conforming to MIL-L-21260 specification.

The fuel intake line shall be disconnected at an accessible point. A portable container with two compartments shall be connected to the fuel intake line. One compartment shall contain fuel conforming to VV-F-800, and the other shall contain Type P-10, Grade 10 preservative oil. The fuel injector return line shall be disconnected at an accessible point and arranged for drainage into a recovery container. Engine shall be started and operated at fast idle until thoroughly warm. The engine shall be accelerated to 3/4 speed at which time the fuel supply shall be switched to portable container containing Type P-10 preservative oil. Engine shall be operated at this speed until undiluted preservative oil is flowing out of fuel injector return line into recovery container. Engine shall be stopped and allowed to cool to either 100°F or to the ambient temperature, if the ambient temperature is greater than 100°F. The intake manifold, exhaust manifold, and valve rocker covers shall be removed. Each intake valve shall be manually depressed, and one-fourth of the predetermined amount of MIL-L-21260 preservative oil shown in Section 3.8 of MIL-E-10062 shall be atomized sprayed past each open inlet valve into the cylinder. Repeat this procedure on the exhaust valve side by depressing each exhaust valve and atomize spray one-fourth of the predetermined amount of MIL-L-21260 preservative oil past each open exhaust valve into the cylinder. Slowly turn over the engine, preventing ignition, one revolution, to spread the preservative oil over the cylinder walls. Repeat the process of depressing each inlet and exhaust valve, and atomize spray one-fourth the amount of preservative oil past each open intake and exhaust valve. Spray exposed valve actuation gear with preservative oil. Reinstall intake manifold, exhaust manifold, and valve rocker cover. Seal all openings into engine, and tag engine as being preserved.

CANDIDATE PROCEDURE "B"

New equipment shall have engine crankcase drained of existing lubricating oil. The drain plug shall be replaced. The engine crankcase shall be filled to the operating level with the correct grade (weight) of preservative lubricating oil conforming to MIL-L-21260 specification.

The fuel intake line shall be disconnected at an accessible point. A portable container with two compartments shall be connected to the fuel intake line. One compartment shall contain fuel conforming to VV-F-800, and the other shall contain Type P-10 preservative oil. The fuel injector return line shall be disconnected at an accessible point and arranged for drainage into a recovery container. Engine shall be started and operated at fast idle until thoroughly warm. The engine shall be accelerated to 3/4 speed at which time the fuel supply shall be switched to portable container containing Type P-10 preservative oil. Engine shall be operated at this speed until undiluted preservative oil is flowing out of fuel injector return line into recovery container. Engine shall be stopped, and tagged as being preserved. Seal all engine openings once engine has cooled to an appropriate temperature.

CANDIDATE PROCEDURE "C"

New equipment shall have engine crankcases drained of existing lubricating oil. The drain plug shall be replaced. The engine crankcase shall be filled to the operating level with the correct grade (weight) of preservative lubricating oil conforming to MIL-L-21260 specification.

The fuel intake line shall be disconnected at an accessible point. A portable container with two compartments shall be connected to the fuel intake line. One compartment shall contain fuel conforming to VV-F-800, and the other shall contain Type P-10 preservative oil. The fuel injector return line shall be disconnected at an accessible point and arranged for drainage into a recovery container. Engine shall be started and operated at fast idle until thoroughly warm. The engine shall be accelerated to 3/4 speed at which time the fuel supply shall be switched to portable container containing Type P-10 preservative oil. Engine shall be operated at this speed until undiluted preservative oil is flowing out of fuel injector return line into recovery container. Engine shall be stopped. Once engine has cooled to an acceptable temperature, the fuel injectors should be removed without disconnecting the fuel supply lines. The fuel supply throttle shall be in the off position. An amount (see Section 3.8 of MIL-E-10062 to determine correct amount) of grade 10, MIL-L-21260 shall be atomize sprayed into each cylinder through the injector hole. The nozzle tip shall be inserted through the hole during the process. The maximum air pressure shall not exceed 25 psi. With injectors removed engine shall be turned through one revolution. Injectors shall be dipped into a container of grade 10, MIL-L-21260 specification preservative oil prior to reinstallation in engine. Seal all engine openings, and tag engine as having been preserved.

CANDIDATE PROCEDURE "D"

New equipment shall have engine crankcases drained of existing lubricating oil. The drain plug shall be replaced. The engine crankcase shall be filled to the operating level with the correct grade (weight) of preservative lubricating oil conforming to the MIL-L-21260 specification.

The fuel intake line shall be disconnected at an accessible point. A portable container with two compartments shall be connected to the fuel intake line. One compartment shall contain fuel conforming to VV-F-800, and the

other shall contain Type P-10 preservative oil. The fuel injector return line shall be disconnected at an accessible point and arranged for drainage into a recovery container. The air inlet shall be disconnected at the point nearest the intake manifold or turbo, as applicable. Engine shall be started and operated at fast idle until thoroughly warm. The engine shall be accelerated to 3/4 speed at which time the fuel supply shall be switched to a portable container containing Type P-10 preservative oil. The engine shall be operated at this speed until the undiluted preservative oil is flowing out of the fuel injector return line into the recovery container. Two minutes prior to engine shutoff begin atomize spraying oil conforming to the crankcase grade of MIL-L-21260 specification preservation oil in through the open intake manifold. After 2 minutes of operation shut off the engine. When the engine has completely stopped, turn off the atomize spray of oil directed into the intake manifold. When the engine has cooled to an acceptable temperature, seal all openings with waterproof tape. Tag the engine as having been preserved.

CANDIDATE PROCEDURE "E"

New equipment shall have engine crankcases drained of existing lubricating oil and the drain plug shall be replaced. The engine crankcase shall be filled to the operating level with the correct grade (weight) of preservative lubricating oil conforming to MIL-L-21260 specification. Operate the engine until it reaches normal operating temperatures, then shut it off.

The engine shall be tagged as being preserved. Seal all engine openings once the engine has cooled to an appropriate temperature.

Analysis of Candidate Preservation Procedures

Each of the candidate preservation procedures are effective over the period of time and condition of storage that they are intended to be used in. This ranges from less than 1 year of indoor storage for Candidate Procedure E to over 1 year of outdoor storage for Candidate Procedure A.

In terms of simplicity, however, there is a great deal of difference between the various candidate procedures. Candidate Procedure A, while providing the maximum protection from corrosion, requires approximately 170% more time to preserve than the next most involved procedure, and 530% more time than the simplest procedure. As a result, Candidate Procedure A results in higher labor costs during preservation compared to the other procedures.

For providing the most cost effective protection during indoor storage of up to 1 year, diesel-powered equipment should be preserved by Candidate Procedure E. This Procedure of changing the oil while using a MIL-L-21260 C specification rust preventing oil, and circulating this oil thoroughly through the engine by operating the engine for 10 minutes, has been well proven by commercial industry for use in equipment or engines which will be stored for less than 1 year. This will preserve and protect the engine by neutralizing any combustion acids present, and by coating all of the lubricated surfaces and the critical portions of the cylinder walls with the oil-carried rust inhibiting additives.

For long-term storage protection from rust or corrosion, both Candidate Procedure B (preservation of cylinders by spraying preservative oil through fuel injectors) and Candidate Procedure D (preservation of cylinders by spraying preservative oil into the air intakes while the engine is running) come closest to providing the protection of MIL-C-10062E(2) level A preservation. Both of these procedures are much simpler to perform than the MIL-C-10052E(2) procedure. However, Candidate Procedure B cannot be used on all diesel engines due to variations in combustion chamber designs and injector spray patterns. These variations can prevent the cylinder walls and combustion chamber surfaces from being adequately coated with preservative oil.

The simplest and most effective alternative procedure which comes closest to providing the protection of the MIL-C-10062E(2) preservation procedures is then Candidate Procedure D. This procedure of spraying preservative oil into the air intakes while the engine is running is used by the Industrial Engines Operations of the Ford Motor Company, by Teledyne Wisconsin Motors in their commercial engines, and was recommended by the Mobil Oil Company. As documented in the trip report at the end of this section, Ford has used this procedure to preserve engines for 4 years of storage with no rust problems.

What happens during the execution of this procedure is the air that enters each cylinder is extremely rich with oil. This air and oil mixture lubricates the inlet valve and valve seat as it passes through the open valve into the cylinder. Once the air and preservative oil mixture is in the cylinder, additional preservative fuel/oil is injected into the cylinder as per normal operation. During compression and injection the air is extremely rich with fuel and oil, and air turbulence or swirl in the cylinder, caused by the orientation of the intake relative to the cylinder and by combustion chamber design, causes some of the preservative fuel/oil to fall out of suspension from the air and

coat the cylinder walls. Because this film on the cylinder walls is not atomized with air it will not support combustion, and thus remains behind on the cylinder and combustion chamber walls after the completion of normal combustion. At this point the exhaust gases are still rich with preservative oil, and thus the exhaust valves and valve seats will be coated with some preservative material by this process.

From the above, and from the description of Candidate Procedure D, it is apparent that this procedure may be used with substantially equal effectiveness on all types of engines. If this procedure was incorporated as a replacement for part of MIL-C-10062E(2), the result would be a simpler and easier to follow procedure which does not significantly change between gasoline or diesel, 2 or 4 stroke, ported or valved, or direct or indirect injection engines.

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